PUSH Bulletin

DuPont FluoroIntermediates

# DuPont HFPO

## *Properties, Uses, Storage, and Handling*

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## Introduction

Hexafluoropropylene oxide (HFPO) is a versatile fluorointermediate that can be used in the synthesis of fluoromonomers, fluoropolymers and to add fluorine functionality to a variety of organic precursors. Perfluorinated vinyl ethers utilized in the production of commercial fluoropolymers are produced using HFPO as the key intermediate. In addition, the commercial perfluorinated Krytox® lubricant has HFPO as the monomer unit. Other useful commercial fluorointermediates produced from HFPO include hexafluoroisopropanol, hexafluoroisobutylene and bisphenol AF. All of these FluoroIntermediates are commercially available through DuPont.

## Properties

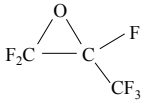
HFPO supplied by DuPont has a minimum purity of 98.6 wt% (**Table 1**). When impurities are detected they generally consist of hexafluoropropene (HFP). HFP is the key chemical precursor to HFPO which is synthesized in an oxidation process. This product may also contain a very low level of hexafluoroacetene (HFA), which is a potential reproduction hazard. The HFA isomer is generated by a metal catalyzed mechanism that can be initiated by improper storage and handling methods. See **Storage** section and MSDS for more information.

Physical properties of HFPO are given in **Table 2**. HFPO is a nonflammable gas that is stored as a pressurized liquid. The vapor pressure equilibrium curve for HFPO is included in **Figure 1**.

**Table 1**
**Product Data**

| Property | Unit | Min. | Max. |
|---|---|---|---|
| Organic Purity – HFPO | Weight % | 98.6 | ——- |
| HFP (Hexafluoropropene) | Weight % | — | 1.0 |

**Table 2**
**Physical Properties**

| Property | Unit | Typical Value |
|---|---|---|
| Chemical Name | — | Oxirane, Trifluoro (Trifluoromethyl) |
| CAS No. | — | 428-59-1 |
| EINECS No. | — | 207-050-4 |
| Chemical Formula | — |  |
| Molecular Weight | — | 166 |
| Boiling Point @ 1 atm | ºC (ºF) | –27 (–17) |
| Vapor Pressure @ 25°C | kPa-abs (psia) | 660 (96) |
| Melting Point | ºC (ºF) | –144 (–227) |
| Liquid Density @ 25°C | kg/m$^3$ (lb/ft$^3$) | 1300 (81.2) |
| Vapor Heat Capacity @ 25°C | J/mol·K | 138 |
| Liquid Heat Capacity @ 25°C | J/mol·K | 172 (estimated) |
| Heat of Vaporization @ NBP | KJ/mol | 21.8 |
| Critical Temperature | ºC (ºF) | 86 (186.8) |
| Critical Pressure | kPa·abs (psia) | 2896 (420) |
| Critical Density | g/cc | 0.59 |
| Flammability Limits | Vol% | None |
| Exposure Limits – HFPO, AEL 8hr. TWA* | ppm | 20 |

* AEL is the DuPont's internally used Acceptable Exposure Limit. Where governmentally imposed occupational exposure limits which are lower than the AEL are in effect, such limits shall take precedence.
TWA = Time weighted average

**Figure 1**

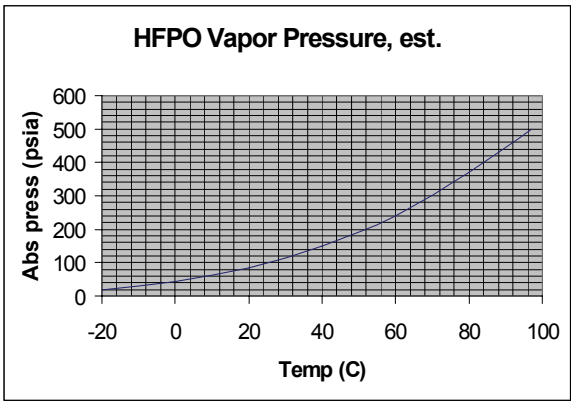



**Figure 2. Infrared Spectrum of Hexafluoropropylene Oxide Vapor at 3.5 kPa in a 10 cm cell**

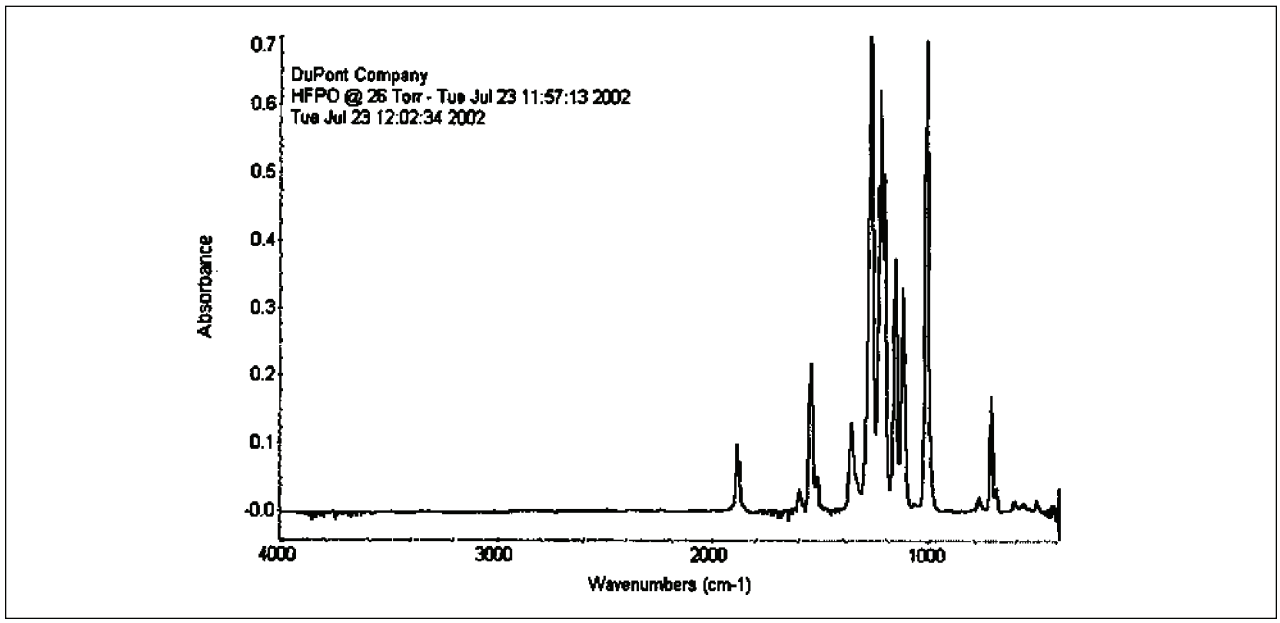
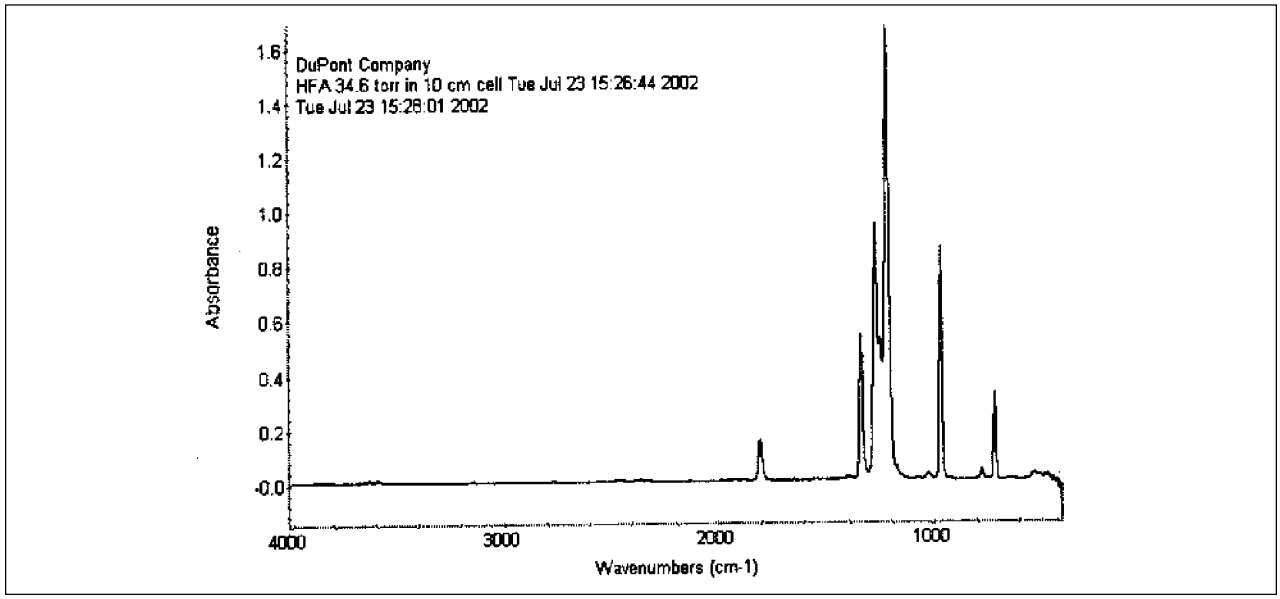



**Figure 3. Infrared Spectrum of Hexafluoroacetone Vapor at 4.6 kPa in a 10 cm cell**



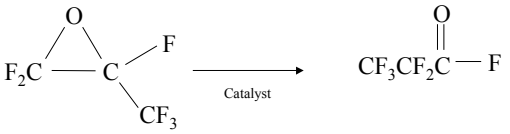
## Uses

Hexafluoropropylene oxide (HFPO) is a key intermediate in the synthesis of organofluorine compounds. Many commercial fluoropolymers use HFPO either as a monomer or a monomer precursor. The epoxide ring is opened by nucleophiles to give a variety of derivatives. HFPO may be isomerized to either pentafluoropropionyl fluoride (PPF) or hexafluoroacetone (HFA). The thermolysis of HFPO can also serve as a source of difluorocarbene. A few examples of HFPO chemistry are given below; the chemistry of HFPO has been reviewed.[1,2]

### *Reactions of HFPO*

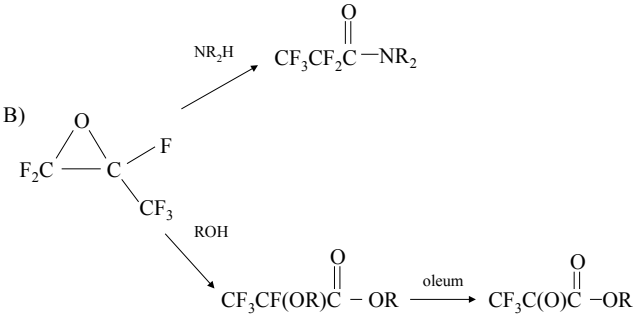
HFPO is easily isomerized to pentafluoropropionyl fluoride (PPF) by nucleophilic catalysts such as halides or amines.[A]

A)



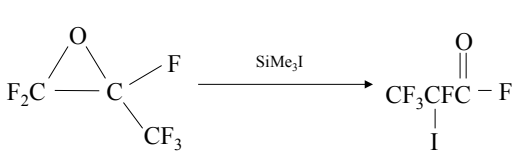

In the presence of alcohols or secondary amines, derivatives of PPF are formed. Methyl 2,3,3,3-tetrafluoro-2-methoxy propionate, prepared from methanol and HFPO, may be converted to methyl 3,3,3-trifluoropyruvate, a useful building block in organofluorine chemistry.[B]

B)



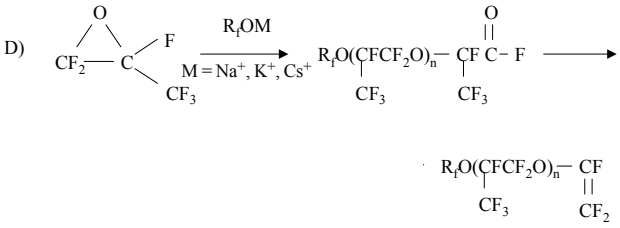

Ring-opening the HFPO with halogenating reagents such as $Me_3SiI$ gives halogenated perfluoroalkylpropionic acid derivatives such as $CF_3CFIC(O)F$.[C]

C)



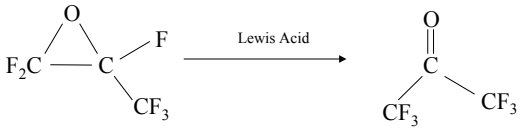

HFPO can serve as a source of the heptafluoropropoxide ion owing to the equilibrium between PPF and fluoride ion in solution. The heptafluoropropoxide ion, as well as other polyfluorinated alkoxides, open the HFPO ring to generate oligomers which can be isolated as the acid fluorides.[D] The acid fluorides in turn may be converted to vinyl ethers which are themselves useful chemical intermediates.

D)



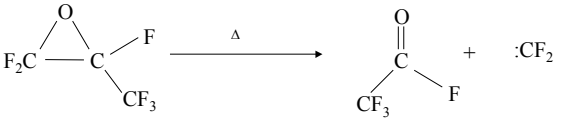

In the presence of Lewis acids such as $SbF_5$, HF or $ACl_xF_{3-x}$ (x = 0.05–0.3), HFPO isomerizes to HFA.[E] This can even happen in storage containers if precautions are not taken to prevent the rearrangement reaction from occurring.

E)




Thermolysis of HFPO gives difluorocarbene and trifluoroacetyl fluoride.[F] The difluorocarbene may be generated *in situ* to prepare useful intermediates such as $CF_2I_2$ or cyclopropanes.

F)



## Storage and Handling

### *Shipping containers in the U.S.*

Hexafluoropropylene oxide is a liquefied, nonflammable compressed gas. According to the U.S. Department of Transportation (DOT), a nonflammable compressed gas is defined as a nonflammable material having an absolute pressure greater than 40 psia at 21ºC (70ºF) and/or an absolute pressure greater than 104 psi at 54ºC (130ºF).

**The appropriate DOT designation is as follows:**

| | |
|---|---|
| Proper shipping name: | Liquefied Gas, N.O.S. Hexafluoropropylene Oxide |
| Hazard Class: | 2.2 |
| UN. No. | 3163 |
| DOT Labels | Nonflammable gas |
| DOT Placards | Nonflammable gas |

**Containers**

| Water Capacity | Dimensions | DOT Specification | Neight Weight HFPO | Liquid Dip Tube | Phase Available |
|---|---|---|---|---|---|
| 760 L | 208 cm L x 76 cm D | 110A500W | 818 kg | Yes | Liq or Vap |
| 760 L | 208 cm L x 76 cm D | 106A500W | 818 kg | Yes | Liq or Vap |
| 17,000 L ISO | 2.4 m x 2.6 m x 6.1 m L (frame) 6.1 m L x 2.4 m OD | 51 | 15,000 kg | Yes | Liq or Vap |

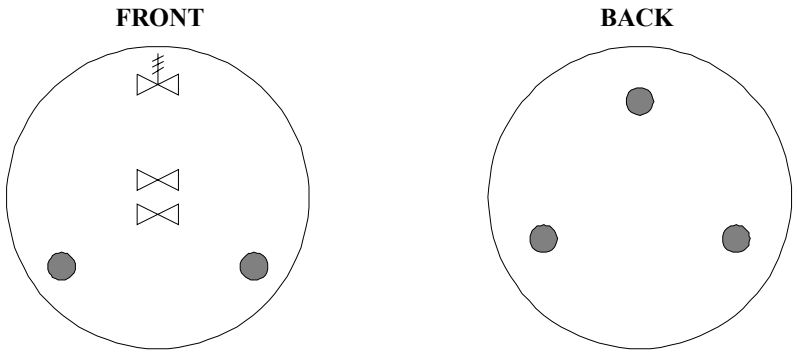
Smaller sizes are available upon request for developmental purposes.

There are two types of 760 L cylinders used for shipping HFPO. They are designated by the DOT specifications 110A500W and 106A500W and are identical in dimensions and only differentiated by the position of the valves, relief valves and plugs.

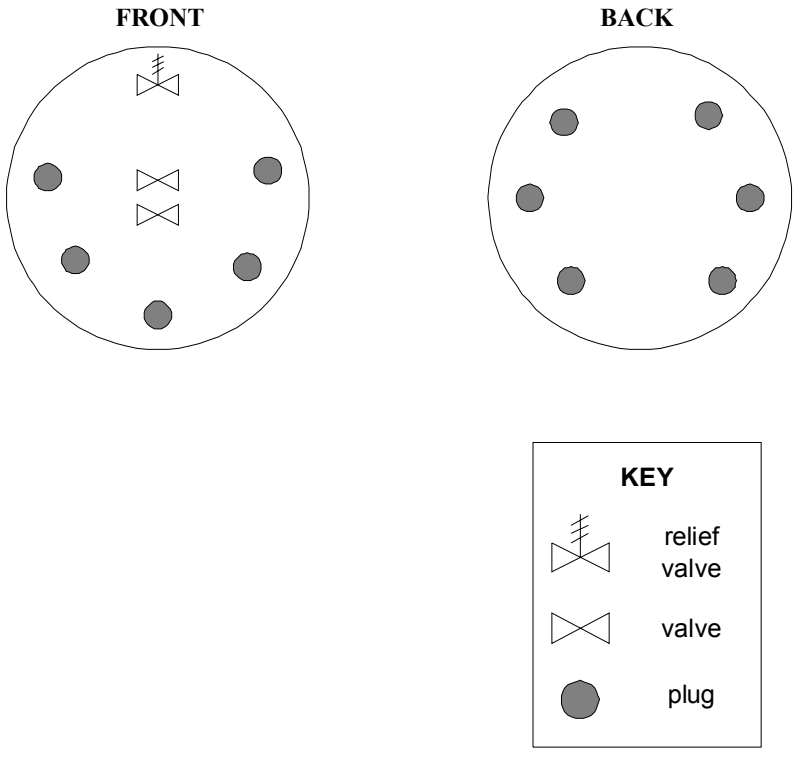
It is important to note the location of the cylinder relief valves (RVs). The relief valve should be positioned along a vertical axis aligned with the cylinder valves such that the cylinder relief valve is at the highest point. This ensures that the RV will pass vapor if venting occurs and it will minimize the amount of liquid remaining in the cylinder after use. The black stripe with “this side up” text is painted on each cylinder to serve as a reminder.

### Valve, Relief Valve, and Plug Placement for 760 L Cylinders

A) 110A500W - Silver with Black Stripe




B) 106A500W - Silver with Black Stripe



## Hexafluoropropylene Oxide Rearrangement Concerns

Hexafluoropropylene oxide can rearrange to the potential reproductive hazard hexafluoroacetone (HFA) in the presence of Lewis acids. This can occur in shipping containers, storage vessels, or other process equipment. Because higher temperatures cause faster rearrangement, it is highly recommended to maintain the HFPO below 25 ºC (77 ºF) unless required for process purposes (i.e. purification or chemistry).

Corrosion by-products in carbon steel containers can catalyze the HFPO rearrangement to HFA. In order to inhibit the rearrangement reaction, toluene is commonly added to carbon steel containers. Low levels of toluene have been shown to be effective as an inhibitor in this rearrangement reaction. If the end user requires even lower levels of toluene, a special low toluene grade can be selected, but it is strongly recommended that shipping containers be constructed of stainless steel when toluene is not intentionally added as an inhibitor.

Because the potential for rearrangement of HFPO to HFA is always present, it is recommended that hexafluoropropylene oxide be treated as though it always contains HFA unless a recent analysis suggests otherwise.

## Material Compatibility Concerns

Most metal components are suitable for use with HFPO; however, corrosion resistant materials such as stainless steel are recommended. If less corrosion resistant materials, such as carbon steel, are used in the process equipment, toluene inhibited HFPO is the preferred product.

## Handling Precautions

The following rules for handling hexafluoropropylene oxide containers are strongly recommended:

1. Use proper personal protective equipment, such as side shield safety glasses, gloves and safety shoes when handling containers.
2. Exposure to HFPO should be prevented or minimized using proper ventilation and chemical hygiene practices.
3. Always treat HFPO containers as though they contain HFA unless a recent analysis indicates otherwise.
4. Use proper backflow prevention methods when connecting and disconnecting HFPO cylinders. Introduction of water into an HFPO cylinder can lead to HFA formation by slowly generating HF, leading to corrosion and ultimately HFA.
5. To reduce the rearrangement of HFPO to HFA, carbon steel cylinders should be maintained below 25ºC (77ºF).
6. To reduce rearrangement of HFPO to HFA, it is recommended that product shipped in carbon steel containers be used within 90 days of shipping..
7. Skin contact with HFPO liquid or escaping vapor can lead to frostbite.
8. Never heat a container to temperatures higher than 45ºC (113ºF).
9. Maintain filled containers with the correct orientation as indicated on cylinders to ensure relief protection is located in the vapor phase.
10. Never apply direct flame or live steam to a container or valve.
11. Never refill disposable cylinders with anything. The shipment of refilled disposable cylinders is prohibited by DOT regulations.
    **NOTE:** Disposable cylinders are often used when supplying lab-scale samples.
12. Never refill returnable cylinders without DuPont consent. DOT regulations forbid the transportation of returnable cylinders refilled without DuPont authorization.
13. Never use a lifting magnet or sling (rope or chain) when handling containers. A crane may be used when a safe cradle or platform is used to hold the container.
14. Never use containers as rollers, supports, or for any other purpose other than originally intended.
15. Protect containers from any object that will result in a cut or other abrasion in the surface of the metal.
16. Never tamper with the safety devices in the valves or containers.
17. Never attempt to repair either containers or valves.
18. Never force connectors that do not fit properly. Make sure threads on the regulators or auxiliary equipment are the same as those on the container valve outlets.
19. Keep valves tightly closed and valve caps and hoods in place when containers are not in use.

**NOTE:** Storage and Handling: Store and handle in accordance with all current regulations and standards subject to storage regulations: U.S. OSHA 29 CFR 1910.101.

## References


1. Tarrant, P.; Allison, C. G.; Barthold, K. P. *Fluorine Chem. Rev*. **1971**, 5, 77-113.
2. Millauer, H.; Schwertfeger, W.; Siegemund, G. *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 161-179.

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